

A novel nano zero-valent iron@chitosan for effective removal of Microcystin-LR: kinetics and adsorption mechanism

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Abstract. Microcystin-LR (MC-LR) is one of the most notorious toxins liberated from cyanobacteria in drinking water sources. In this study, a skillful method access to new nanozero-valent iron @chitosan (nZVIMC) was synthesized by a facile one step method. The as-prepared nZVIMC was employed as an adsorbent for the effective removal MC-LR from aqueous solution. Transmission electron microscopy (TEM) demonstrates that nZVIMC is in quasi-spherical shape with size of around 50 nm, effect of variable parameters such as pH, contact time, initial concentration of MC-LR and adsorption properties of nZVIMC on MC-LR was further investigated. Scanning electron microscope (SEM) reveals that the particles are nearly spherical in shape with agglomeration. The results indicated that good adsorption performance was achieved at an initial pH of 5. The adsorption kinetics of nZVIMC was better fitted by pseudo-secondorder kinetics. The adsorption isotherm data was fitted well to Langmuir isotherm and then to Freundlich model, with an adsorption capacity of 68.9 mg/g at 300K. Thus, we believe that nZVIMC can be used as a low cost material for efficient removal of MC-LR from water.

1 Introduction

Algal bloom caused by eutrophication has grown up to be a serious environmental problem, such as the Taihu lake pollution incident encountered in Wuxi city of China during 2007^[1]. Microcystin-LR (MC-LR) is a part of the deadliest algae toxins produced by cyanobacteria^[2]. The World Health Organization has set a safe guideline value of 1.0µg/L of MC-LR in daily drinking water^[3,4]. The toxicity of MC-LR is explained by their strong binding and inhibition of protein phosphatases. MC-LR is also known to promote the growth of tumor and has a genotypic effect as well as strong mutagenicity. Long term consumption of MC-LR contaminated water may induce liver damage, liver cancer, and even death in humans^[5,6].

Although inhibiting Microcystis (MCs) growth in water resources is the most effective method to reduce MCs, it needs long-term investment. Therefore, expeditious removal of MCs is another option. Although variety of treatment methods, including activated carbon absorption, potassium permanganate oxidation, TiO₂ photocatalytic oxidation, and sand filter biodegradation have been reported for the removal of MCs [add reference], some appreciable disadvantages have been identified. Removal of MC-LR by activated carbon is a simple and effective technology, but the removal efficiency is significantly reduced in natural water sources due to the presence of other organics^[7]. Treatment with potassium permanganate could destroy

MCs quickly; however, it easily interferes with unsaturated compounds, which lead to rapid depletion of potassium permanganate and incomplete oxidation of MCs^[8]. Though most of the MCs in waters are eliminated through biodegradation^[9-10], the process takes long time to implement this technology in practical water treatment process.

The aim of this research was tantamount to design a new material for removal of MCs with high efficiency and to reduce risk to human health. The prepared material is rapid, cost-effective and reproducible.

2 Materials

MC-LR and FeCl₃·6H₂O (Ferric tetrachloride) were purchased from Sigma-Aldrich; chitosan with a deacetylation degree of 80-95% was purchased from Sino pharm Chemical Reagent Co.Ltd., China. All other chemicals were of analytical grade and deionized water was used for all experiments. Required concentrations of the standard solution were obtained by diluting stock solution with double distilled water.

2.1 Preparation of nZVIMC

The synthesis of nZVIMC was induced by chitosan hydrogel via in-situ co-precipitation method at low temperature and normal atmosphere. Chitosan hydrogel was prepared by dissolving 0.5 g of chitosan in 200 mL

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of 0.5% (v/v) acetic acid solution with continuous stirring. 5.2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, were dissolved in 50 mL of distilled water, and honey was added dropwise as a reducing agent to convert Fe^{3+} to Fe^0 , then the mixture was stirred vigorously for 30 min. Chitosan hydrogel were added to Fe^0 solution by stirring at 3000 rpm for 10 min in a water bath at 40°C to form chitosan-iron ions composites. It was provided sufficient time and proper conditions for chitosan to chelate iron ions. After stirring, the obtained product was washed three times with ethanol and filtered. The obtained product was dried in a vacuum oven at 90°C for overnight and the final product was stored in a stoppered bottle.

2.2 Adsorbent Characterization

Morphology and grain size of nZVIMC were examined by a Tecnai G20 TEM (FEI, USA) and S4800 SEM (Hitachi, Japan). Magnetic behavior of the nanoparticles sample was obtained by a MPMS-XL-7 magnetic measurement instrument (quantum design, USA).

2.3 Adsorption experiments

All the adsorption tests were conducted in 250mL conical flasks. For adsorption kinetics, 1 mg of nZVIMC was added to 100mL of MC-LR ($300\mu\text{g/L}$) and shaken at 150 rpm (25°C) for 120min. while for adsorption isotherms test, 1 mg of nZVIMC was added to 50-1000 $\mu\text{g/L}$ of MC-LR in a conical flask and was shaken for 120 min at 150 rpm and at 25°C of temperature. The adsorption equilibrium time was based on the results of adsorption kinetics. The concentration of MC-LR was identified by high performance liquid chromatography tandem mass spectrometry [11].

The effect of pH on MC-LR adsorption was investigated by adjusting the initial solution pH from 2 to 12 using 0.1 mol/L HCl and 0.1mol/L NaOH with initial MC-LR concentration of $300\mu\text{g/L}$. Zeta potentials were measured with a Zetasizer Nano ZS90 instrument (Malven Instruments Ltd., UK).

3 Results and Discussion

3.1 Characterization of nZVIMC

As shown in Fig.1, the isoelectric point of nZVIMC was pH 7.8. the morphology of synthesized nZVIMC was investigated by TEM and SEM imaging as shown in Fig.2. From the figure it indicates that nZVIMC particles are in quasi-spherical in shape with size of around 50 nm (Fig. 2a). From SEM images (Fig. 2b) it indicates that there is a slight aggregation of these nanoparticles due to the existence of cross-linked chitosan on the surface of nZVIMC.

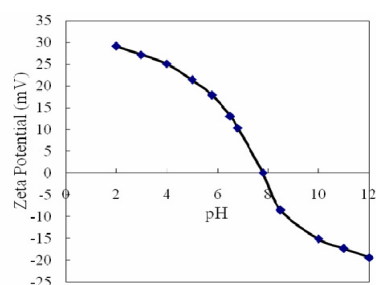


Fig.1. Zeta potential of nZVIMC (1g/L) as a function of pH.

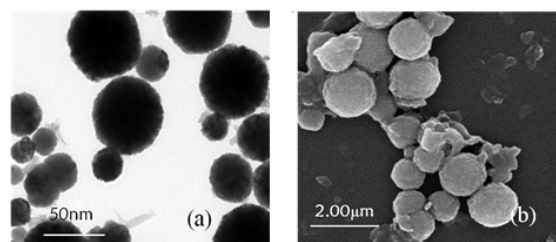


Fig. 2. TEM (a) and SEM (b) images of nZVIMC.

Magnetic behavior of the nanoparticles sample was obtained using a MPMS-XL-7 magnetic measurement instrument (Quantum Design, USA). The super paramagnetic character of nZVIMC is evident from the nanoparticles magnetic hysteresis loop as shown in Fig. 3. The nanoparticles saturation magnetization was 59.53 emu/g. This demonstrated that the adsorbent can be separated from its aqueous dispersion easily in a few minutes using an external applied magnetic field.

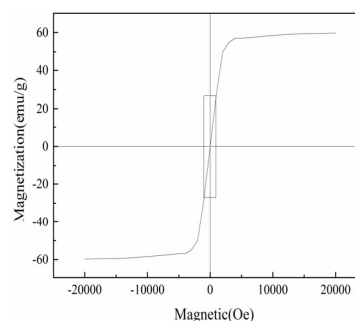


Fig.3. Magnetic hysteresis loop of nZVIMC.

Adsorption time is the key parameter because it can reflect the adsorption kinetics of an adsorbent. Fig.2a shows the contact time profile of MC-LR removal of nZVIMC. The adsorption amount of MC-LR increased sharply within the first 1 h of contact time, after which was slowed down. This phenomenon may be the adsorption sites were void and adsorbates could be easily interacted with these sites during the initial stage. With increase in time the remaining vacant sites are not easily occupied, until the system reached equilibrium.

To determine the adsorption kinetics of MC-LR on the nanoparticles, two kinetic models were applied to fit the experimental data. Pseudo-first-order and pseudo-second-order which were used to explain the solid/liquid adsorption.

In order to investigate the controlling mechanism of the adsorption process, the adsorption/time data obtained

were applied to three kinetic models, including the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model [12, 13]. The Lagergren equation was used as the pseudo-first-order kinetic model by the following equation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where q_e and q_t (mg/g) are the amount of MC-LR adsorbed on ACMCSM at equilibrium and at a given time t , respectively; k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order kinetic model was as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where k_2 ($\text{g}/(\text{mg min})$) is the adsorption rate constant of the pseudo-second-order.

The intraparticle diffusion model was given by the follows:

$$q_t = k_p t^{1/2} + C \quad (3)$$

where q_e ($\text{mg/g min}^{0.5}$) is the intraparticle diffusion rate constant and C of adsorption constant is the intercept.

Table 1. Best-Fit Model for MC-LR Adsorption on nZVIMC

	Param.1	Param.2	R ²
First-order	$q_e(\text{mg/g})=28.75$	$k_1=0.005$	0.941
Second-order	$q_e(\text{mg/g})=48.38$	$k_2=0.017$	0.997
Intraparticle	/	$K_p=3.049$	0.893
Langmuir	$q_m(\text{mg/g})=72.99$	$b=0.0995$	0.997
Freundlich	$K_F=12.9591$	$n=2.592$	0.944

The results of the kinetics were obtained by analyzing Fig.4. Based on the correlation coefficients, the pseudo-second-order kinetic equation with $R^2 > 0.99$ was feasible to describe the adsorption process, as shown in Table 1. This suggests that the overall process seems to be controlled by chemisorption without any mass transfer in the solution [12]. These results are in good agreement with the adsorbing pharmaceuticals in drinking water [14].

3.2 Adsorption isotherm

In order to interpret the adsorption data, Langmuir and Freundlich adsorption isotherm models were used to describe the equilibrium adsorption for MC-LR on nZVIMC.

Linearized Langmuir equation is [15]:

$$\frac{c_e}{q_e} = \frac{1}{b q_m} + \frac{c_e}{q_m} \quad (4)$$

Where q_e and c_e are the amount adsorbed (mg/g) and the adsorbate concentration in solution (mg/L), both at equilibrium b (L/mg) is a constant related to the heat of adsorption and q_m (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent.

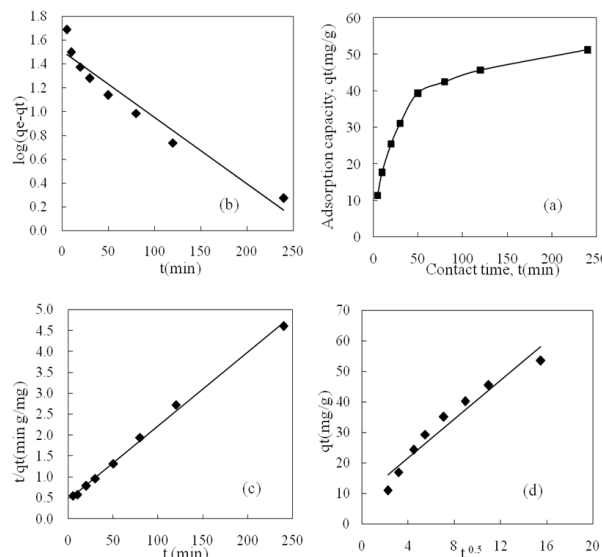


Fig.4. Effect of contact time on MC-LR adsorption (a); fitting pseudo-first-order kinetic plots (b & c) and intra-particle diffusion kinetic plots (d) of MC-LR adsorption, in which t is the reaction time (min) and qt (mg/g) is the amount of adsorbed fluoride at a particular reaction time t .

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems in which the model is expressed by the following equation [16]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where K_F is Freundlich constant and n is the heterogeneity factor.

The theoretical parameters of adsorption isotherms along with regression coefficients are summarized in Table 1. From the two studied systems (Fig 5), the Langmuir isotherm model correlated better ($R^2 > 0.99$) than Freundlich isotherm with the experimental data from adsorption equilibrium of MC-LR by MACFM. The maximum adsorption values were in good accordance with experimentally obtained values. The fact that the Langmuir isotherm model assumes monolayer adsorption on a surface with a finite number of identical sites, these sites are energetically equivalent and there is no interaction between adsorbed molecules. It has been reported that the values of n in the range 1-10 indicates favorable condition for adsorption [17]. In the present work, the exponent was around 2.592, predicting the adsorption system is well.

The removal efficiency of toxins was calculated based on the adsorption isotherm kinetics. Approximately 90% of toxins were removed at the concentrations ranging from 50 to 500 $\mu\text{g/L}$. which is same as the reported toxin levels in drinking water [11]. The removal efficiency was comparable with other chemical or biological methods [18, 19], satisfied the maximum allowable concentration (1000ng/L) prescribed by the world health organization (WHO) in human drinking water [5].

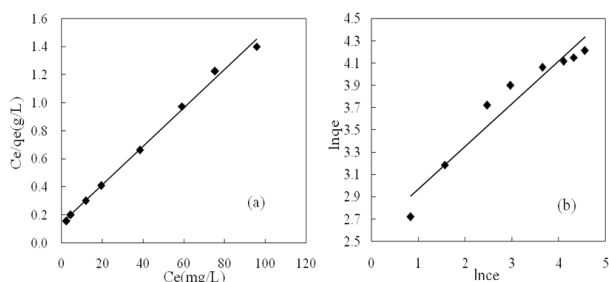


Fig.5. Linear plots of Langmuir (a) and Freundlich adsorption isotherm (b).

3.3 Effect of solution pH on MC-LR adsorption

As an important parameter in water chemistry, pH can significantly affect MC-LR adsorption. We could know from Fig.6 that as the pH increased, positive charge of MACFM decreased and negative charged increased. While above pH 2.1 MC-LR was negative charged^[20], MC-LR was easily removed, because nZVIMC and MC-LR own the opposite charge to attract each other except at pH2. In addition, under acidic conditions, the hydrophobicity of MC-LR and nZVIMC was much stronger than in alkaline conditions. The similar hydrophobicities of these molecules under acidic conditions may also contribute to the high removal efficiency.

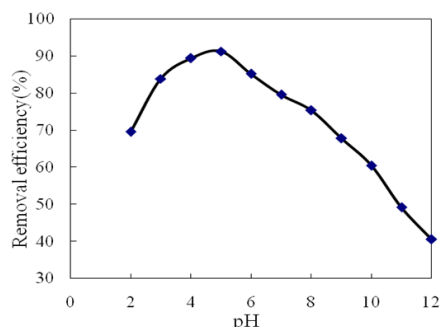


Fig.6. Effect of pH on MC-LR removal efficiency (initial MC-LR concentration 300 μ g/L; temperature 25 $^{\circ}$ C; contact time 60min) at the different pH.

4 Conclusion

We have synthesized a core-shell type nZVIMC, with a magnetic core and carboxymethyl cellulose shell decorated with zero iron for effective removal of MC-LR from water as an eco-friendly and cost-effective water purification technique. The magnetite carboxymethyl cellulose microspheres displayed a spherical shape with Fe₀ decorated on the surface of the microsphere. The mechanism for the adsorption involved electrostatic interaction, hydrogen bonding and complex action reaction. The optimum pH range for MC-LR removal was from 3 to 9 and the interference by natural organic matter was low, demonstrating that this adsorbent can be used in a natural water environment.

Acknowledgments

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